RAW MATERIALS

CRYSTALLIZATION OF MELTS OF WASTE PYROXENE SKARN FROM THE KOITASHSKOE ORE FIELD

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The effect of the cooling rate of melts of pyroxene waste from the Koitashskoe ore field on the type of crystallization is demonstrated. It is established that pyroxene skarn melts have sufficiently high crystallization capacity and with additional introduction of crystallization stimulators can be used in production of glass ceramics with a finely disperse structure.

Crystallization of silicate melts has long been an object of research. A variety of publications on crystallization show the complexity of this process, which depends on the origin of the material studied, as well as on a number of external factors: atmosphere, temperature and exposure in melting and crystallization, presence of impurities, viscosity, pressure, etc. However, despite difficulties, studying crystallization of melts of individual minerals, rocks, and complex mixtures has great theoretical and practical significance.

We selected pyroxene waste from the Koitashskoe ore field, as pyroxene is the main phase of cast articles ensuring their main properties: acid resistance and mechanical strength. Data on the chemical and mineralogical composition of the waste are given in [1].

We investigated the effect of the cooling rate of pyroxene waste melt produced by melting in a solar furnace on the nature of their crystallization. For this purpose we used melted samples obtained by cooling a petrurgical melt at different rates by discharging melt into water and by solidifying on a water-cooled substrate. In the first case, the melt solidified in the form of small drops or spherulites and in the second case in the form of a plate 10 – 30 mm thick (depending on the volume of the melt tank). The melt was also discharged into a sand mold, in which it solidified in the form of a block of 1-liter volume. Solidification lasted 10 min. Samples for analysis were cut out from different parts of the block, from the middle and from the edges. It should be noted that the resulting block was rather brittle, contained large cavities, and could be easily fractured on applying a slight force.

Samples were investigated by x-ray phase (a DRON-UM-1 diffractometer) and crystal-optical (clear sections, a MIN-8 microscope) analysis methods.

The absence of reflections in diffraction patterns of solidifying samples indicated their x-ray amorphousness. Castings obtained by discharging melt into water represented amorphous vitreous material of a greenish-yellow color with a flawed surface and contained a large quantity of gas bubbles of different sizes from 0.05 to 0.11 mm (Fig. 1*a*). The bubbles were mostly hollow; however, in some bubbles opaque inclusions were observed of size 0.002 mm, presumably of iron oxide. These inclusions occupied a certain part, sticking to one side of the bubble. There were also bubbles in which inclusions took the central part. In this case, a rim of a light-colored vitreous mixture was observed along the gas bubble contour, which was less dense than the main mixture, depleted of iron oxide, and more acidic. Furthermore, some darker-colored glass varieties were seen on the surface of the main vitreous mixture, whose composition approached a base composition. Sometimes the base vitreous phase was located inside cracks formed due to abrupt cooling of the sample. The quantity of the darker vitreous material did not exceed 5% of the casting volume.

Castings obtained on a water-cooled substrate presented the following picture. The main material was also vitreous. Gas inclusions were distributed nonuniformly, and their main clusters were registered in the upper part of the plate that was the most remote from the chilled surface. The cumulus phase of the casting in the same part acquired crystalline contours; crystalline aggregates of several varieties of pyroxene were seen, among them ferrous varieties of the type of augite and hedenbergite prevailed, although orthopyroxene (hypersthene $(Mg, Fe)SiO_3$) were found as well. Sites of base glass

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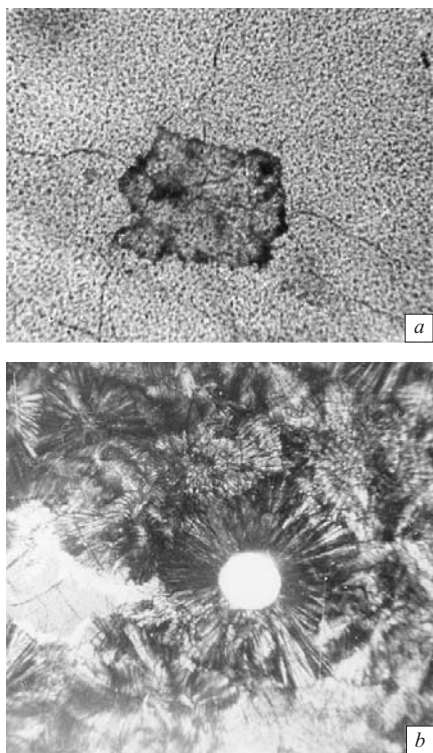
Fig. 1. Microphotos of melted pyroxene skarn: *a*) casting produced by discharging melt into water (× 80, transient light, parallel nicols); *b*) glass ceramic material, annealing at 850°C (× 80, transient light, crossed nicols).

were distinguished against the background of the main close-grained vitreous phase, whereas the rest of the casting had a more homogeneous nature. Such a microstructure fully reflects the effect of the temperature gradient on the type of crystallization.

The microstructure of different zones (the outer and central ones) was compared in the block obtained by discharging melt into a sand mold.

The microstructure of the outer edge is represented by a rather homogeneous vitreous phase, although an initial state of liquation was registered. Similarly as in the casting obtained by discharging melt into water, gas bubbles existed in this block, in which spherical or sharp-angle formations were observed. No crystalline formations were identified. As for the central part of the casting, the beginning of crystallization of pyroxene was observed in it, although there were no traces of liquation. Apparently, ferrous pyroxene crystals were formed on the main sites of the liquating vitreous phase. Some crystalline inclusions acquired a prismatic shape. The reddish tint of the crystallites pointed to an intense oxidation of iron. The amount of the crystalline phase was 3 – 5%.

The thermogram of pyroxene skarn (a Q-1500D derivatograph) exhibits an endothermic peak at a temperature of 850°C caused by heat absorption before crystallization, whereas the beginning of formation of the first crystalline phase relates to 970°C. Kitaigorodskii and Khodakovskaya [2]

believe that the precrystallization period is significant in accelerated crystallization of glasses and its temperature conditions have a strong effect on subsequent crystallization of the glass.

The precrystallization period is the entire temperature interval below the temperature of the formation of the first crystalline phase. One should note the absence of a sharp boundary between the processes occurring in glass in the precrystallization period and during the crystallization stage. Under certain exposures, crystallization centers may emerge within the precrystallization temperature interval of the precrystallization period. Furthermore, a protracted treatment in the precrystallization period may in the end result in crystallization of the glass. This is mostly true of the upper temperatures of the precrystallization periods (the ascending branch of the exothermic effect). The exothermic peaks at a temperature of 990°C correlate with mass crystallization of pyroxene.

The castings obtained were annealed at different temperatures. It is established that a decreased rate of cooling brings the starting temperature of crystallization down from 970 to 900°C.

Microstructure analysis of castings crystallized during 1 h at a temperature of 850°C, i.e., within the precrystallization period, indicated that all samples had a glass-ceramic structure.

Casting obtained by discharging melt into water after annealing contained about 80% crystalline phase. The quantity of that phase in other samples reached 90%. Pyroxene was represented by closely intergrown spherulites with a clearly expressed radial structure, in which diversely oriented thin needles consisting of the finest (1 – 2 μm) crystallites radiated from one crystallization center (Fig. 1*b*). The size of the spherulites reached 500 μm.

It should be noted that the process of crystallization of pyroxenes, as a rule, proceeds for 0.5 – 1.0 h within a rather narrow temperature interval of 850 – 1000°C. The main part of pyroxene is formed in this period. A further increase in exposure duration up to 3 h and the raising of annealing temperature up to 1050°C does not lead to perceptible growth in the content of pyroxene in the castings.

According to data in [3], the first crystalline phase in ferrous aluminosilicate melts is magnetite, which acts as a crystallization center. This is due to the fact that its crystallization capacity is the highest. This mineral crystallizes almost completely in the first 5 min of cooling of the melt. Hedenbergite and augite crystallize at an almost equal rate (60 – 70 and 60 – 65% crystal in the same time interval).

It was earlier demonstrated by means of petrochemical calculations [4, 5] that the composition of melted pyroxene skarn tailings correlates with field III of the cation diagram [3], which, as the authors believe, allows for the formation of finely crystalline glass ceramics of a magnetite-pyroxene structure. At the same time, it should be taken into account that with a ratio of ions in the material of $Ca^{2+} : Mg^{2+} > 1$,

iron ions to a certain degree can be assimilated by pyroxene [3]. In this case, magnetite may be absent, or its quantity will be so small that its identification will be beyond the sensitivity level of some methods of analysis, in particular, x-ray phase analysis.

The diffraction patterns of crystalline samples, regardless of annealing temperature, exhibited pyroxenes (diopside-like hedenbergite and augite) as the main phase and also a small amount of free silicon dioxide. Reflections of magnetite were absent in the diffraction patterns. The blurred shape of the main exothermic effect also points to an insufficient amount of magnetite crystallization centers and a low rate of volume crystallization. However, considering the form of the crystalline pyroxene formation, which points to epitaxial crystallization where crystallites of ferrous monoclinic pyroxene start growing around magnetite grains, it can be assumed that very fine magnetite crystals originally formed in the course of crystallization dissolve in emerging pyroxene.

The performed studies indicated that pyroxene skarn melts have a sufficiently high crystallization capacity and with additional introduction of crystallization stimulators can be used to obtain glass ceramics with a finely disperse structure.

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